



TITLE:

Synthesis of Acetic Acid from Methanol and Carbon Monoxide under High Pressure

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ABSTRACTS

constant rate of extension (v) depends largely upon viscosity (η) and surface tension (γ) as well as temperature. Assuming that the apparent relaxation time can be given by a balance between viscosity and surface tension, the spinning condition was derived as follows:

$$\eta \geq \gamma/v.$$

The spinning temperature expected from the above relation showed a good agreement with the experimental results.

Dielectric Properties of Polyethylene Glycols at Microwave Frequencies

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Journal of Chemical Physics, **27**, 625 (1957)

The complex dielectric constants of ethylene, diethylene, triethylene, tetraethylene, and hexaethylene glycols in the liquid state have been measured at frequencies of 1.43, 9.73, and 18.7 kmc/sec at temperatures from 5 to 50°C. The parameters of dielectric relaxation for these polyethylene glycols have been calculated from the complex dielectric constants and the static dielectric constants by the circular arc rule of Cole and Cole. It has been found that the dielectric relaxation times obtained do not vary much with the homolog of this polyethylene glycol series, being of the order of 10^{-10} sec at 20°C. The value of relaxation time is the largest for diethylene glycol, decreasing slightly with higher homologs of this series. This striking feature is discussed in terms of flexibility of the polyoxyethylene chain due to internal rotation around the C-O bonds of the chain skeleton, which would make more possible a partial and independent orientation of the hydroxyl groups at the ends of the molecular chain in the case of higher polyethylene glycols.

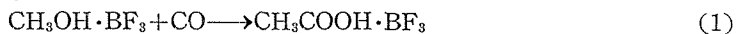
Synthesis of Acetic Acid from Methanol and Carbon Monoxide under High Pressure

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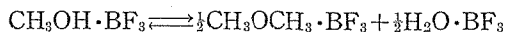
Kinetic studies were made on the synthesis of acetic acid by the reaction of $\text{CH}_3\text{OH} \cdot \text{BF}_3$ with carbon monoxide under high pressure, the main course being expressed by



ABSTRACTS

Based on the observed facts described below a rate expression was derived which could well explain the influence of experimental variables.

1. Besides the main reaction (1), the dehydration of $\text{CH}_3\text{OH}\cdot\text{BF}_3$, producing dimethyl ether and water, occurs, *i. e.*



Since this equilibrium is quickly attainable, $\text{CH}_3\text{OH}\cdot\text{BF}_3$ is reproduced by the reverse shift according as the consumption of $\text{CH}_3\text{OH}\cdot\text{BF}_3$ proceeds by the reaction with CO, which then reacts successively with CO to produce $\text{CH}_3\text{COOH}\cdot\text{BF}_3$.

Thus the addition of $\text{H}_2\text{O}\cdot\text{BF}_3$ to the reactant leads to the increase of initial rate of $\text{CH}_3\text{COOH}\cdot\text{BF}_3$ production (based on charged $\text{CH}_3\text{OH}\cdot\text{BF}_3$). For example, 1.5 : 1 mole ratio mixture of $\text{H}_2\text{O}\cdot\text{BF}_3$ and $\text{CH}_3\text{OH}\cdot\text{BF}_3$ gives 90 mole % yield of $\text{CH}_3\text{COOH}\cdot\text{BF}_3$ in $1\frac{3}{4}$ hours under 1100atm. of CO at 200°C, while 1 : 1 mole ratio mixture of $\text{H}_2\text{O}\cdot\text{BF}_3$ and $\text{CH}_3\text{OH}\cdot\text{BF}_3$ takes nearly $5\frac{1}{2}$ hrs. to reach 90 mole % yield under the same condition.

2. When 1.5 : 1 mole ratio mixture of $\text{H}_2\text{O}\cdot\text{BF}_3$ and $\text{CH}_3\text{OH}\cdot\text{BF}_3$ is used as the starting material under about 1000atm. of CO, the optimum reaction temperature lies at 200°C.

If the reaction temperature is raised to about 210°C, quick occurrence of the side reaction to produce a tarry matter reduces the final yield of $\text{CH}_3\text{COO}\cdot\text{BF}_3$.

3. The result of the experiment on the effect of pressure at 200°C, when 1.5 mole ratio mixture of $\text{H}_2\text{O}\cdot\text{BF}_3$ and $\text{CH}_3\text{OH}\cdot\text{BF}_3$ is used, shows that the yield of $\text{CH}_3\text{COOH}\cdot\text{BF}_3$ is 93 mole % in 2 hrs. in the case of 1100 atm. of CO, and 86 mole % in 7 hrs. in the case of 455 atm.

4. Reaction rate can be expressed by the next formula (3) very well:

$$dy/dt = k \cdot x \cdot f_{\text{CO}}, \quad (3)$$

where, x = existing $\text{CH}_3\text{OH}\cdot\text{BF}_3$ (mole)/charged $\text{CH}_3\text{OH}\cdot\text{BF}_3$ (mole), under equilibrium with ether and water, y = produced $\text{CH}_3\text{COOH}\cdot\text{BF}_3$ (mole)/charged $\text{CH}_3\text{OH}\cdot\text{BF}_3$ (mole), f_{CO} = fugacity of CO, k = rate constant.

k 's are calculated to be $1.7 \times 10^{-5} \text{ atm.}^{-1} \text{ min.}^{-1}$ at 200°C, $0.89 \times 10^{-5} \text{ atm.}^{-1} \text{ min.}^{-1}$ at 180°C, $0.33 \times 10^{-5} \text{ atm.}^{-1} \text{ min.}^{-1}$ at 160°C, and the activation energy is obtained to be 15 Kcal/mole.

Studies on the Coefficient of Kinetic Friction of Fiber

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Report of the Japan Institute for Research on Chemical Fibers, Kyoto Univ.
(*Kasen Koenshu*) 14, 53 (1957)

The apparatus to estimate the coefficient of static and kinetic friction of fibers based upon the Röder's method [H.L. Röder, *J. Text. Inst.*, 44, T 247 (1953)] was constructed. With this apparatus coefficients of static and kinetic